

# **ELECTROCHEMICAL REDUCTION OF FORMALDEHYDE TO ETHYLENE GLYCOL AT MODIFIED GRAPHITE ELECTRODES.**

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## **INTRODUCTION**

Organic electrosynthesis is a very active area of research and in some cases is used for the large scale production of chemicals with the electrodimeration of acrylonitrile to adiponitrile as a well known example [1]. This highly successful process demonstrates that it is possible to envision to use of electrochemistry for the synthesis of other important chemicals either at large scale or at smaller scale for specialty compounds. About a decade ago, a few groups became interested in the electrochemical production of ethylene glycol from formaldehyde [2,3]. Ethylene glycol is used industrially for the production of polyesters and as antifreeze. Therefore, the development of an electrochemical process that is efficient, cost-effective and which also do not rely as much on oil by-products is attractive.

In the earlier studies it was found that only graphitic are efficient electrode materials for the electrochemical reduction of formaldehyde to ethylene glycol [2]. This selectivity was attributed to the presence of oxygen functionalities at the surface of the electrode. Recently, we have shown that oxygen functionalities can be generated at randomly oriented graphite electrodes [4] but that a long-term stability of these graphite electrodes is lacking when used for the electrohydrodimeration of formaldehyde [5].

In this work, we wish to report our results on the use of modified graphite electrodes for the electrosynthesis of ethylene glycol. Graphite electrodes were modified with with the aim to increase the stability of the graphite electrode in organic electrosynthesis. In this work, graphite electrodes were modified with substituted phenyl groups [6] and with a boron-doped diamond coating [7].

## **EXPERIMENTAL**

Randomly oriented graphite electrodes, ATJ and Stackpole 2020 (SP), used in this study were from a commercial source, obtained from UCAR Carbon Co. (Ville d'Anjou, Québec), Inc. and Carbon of America (Toronto), respectively. The graphite electrodes were modified by electrochemical reduction at - 0.7 V for 4 min. of a 5 mM (4-carboxyphenyl)diazonium tetrafluoroborate/acetonitrile solution (6). The diamond layer was prepared according to a published procedure (7).

## **RESULTS AND DISCUSSION**

In a previous study (5) we have observed a decrease of the current efficiency for ethylene glycol production with time (or charge passed during the electrosynthesis). In that study, a flow cell similar to that described previously (2) was used with graphite (ATJ and SP) as cathode materials. The decrease of the current efficiency could be related to

the inhibition effect of methanol and high concentration of ethylene glycol. In some instances, a mechanical desintegration of graphite particles was also clearly noticeable. In order to improve the mechanical stability of graphite electrodes, two different types of "coatings" were generated at their surfaces; a boron-doped diamond layer and a 4-carboxyphenyl group.

In the present study a two-compartment H-cell was used for the experiments. The current efficiency for the unmodified ATJ and SP electrodes is close to 100 % after an initial 5 kC of charge was consumed. Further electrolysis led to a monotoneous decrease of the current efficiency and a value of about 50 % is reached after 50 kC of charge. These results are in agreement with those reported previously in the literature [2].

In contrast to the bare graphite electrode, a boron doped diamond coated SP graphite electrode displays a nearly current efficiency of 100% up to a charge of 50 kC, when the electrolysis was terminated. The fact that a current efficiency of 100% is maintained with a diamond coated graphite electrode suggests that the nature of the electrode material is very important to achieve good performance. The observation of such a high efficiency is also surprising since the presence of oxygen functionalities is thought to be essential for an efficient electrodimmerization of formaldehyde and were required for the proposed reaction mechanism (2). The concentration and nature of oxygen functionalities differ substantially for graphite and diamond surfaces.

Scanning electron micrographs of the diamond coated graphite electrode after an electrolysis of 50 kC revealed that the diamond layer was removed from the surface in some areas. This result was expected because the adhesion of diamond layer is not optimized yet and has been reported previously []. The improvement of the adhesion of diamond coating on various non conducting or conducting substrates is currently underway in one of our laboratory (). The presence of diamond on the surface both at the beginning and after electrolysis was confirmed by Raman spectroscopy. The diamond peak was observed at ??? in both cases.

A similar stabilization of the current efficiency was observed with the 4-carboxyphenyl modified ATJ graphite as the current efficiency also remains close to 100% for an electrolysis of 50 kC. This result is very surprising since this electrode is placed in very aggressive conditions during the electrolysis and it is not clear that the substituted phenyl group can remain on the electrode surface in these conditions. On the other hand, the presence of carboxylic groups might be beneficial for the process at least at the beginning of the electrolysis.

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